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ZERT Final Scientific Report

Los Alamos National Laboratory

EXECUTIVE SUMMARY:

Los Alamos National Laboratory's (LANL) activities for the Center for Zero Emission Research and Technology (ZERT) have fallen into three broad research areas:

- How do you reduce uncertainty in assuring prior to operation that an engineered geologic site will meet a specific performance goal (*e.g.*, <0.01% leak per year)?
- What are key monitoring needs for verifying that an engineered geologic site is meeting a performance goal?
- What are potential vulnerabilities for breeches in containment of CO₂, and how could they be mitigated either prior to operation or in the event that a threshold is exceeded?

We have utilized LANL's multi-disciplinary expertise and an integrated approach combining laboratory experiments, field observations and numerical simulations to address various research issues related to above-mentioned areas. While there have been a number of major milestones achieved as described in past quarterly reports, two of the major accomplishments resulting from LANL's efforts include:

- Development of the CO₂-PENS systems framework for long-term performance analysis of geologic CO₂ sequestration sites. CO₂-PENS is first-ever systems analysis tool designed for assessment of CO₂ sequestration sites.
- One of the few field studies to-date focused on understanding impact of CO₂ leakage on shallow groundwater chemistry. Two major conclusions of the study are as follows: the impact of co-contaminants transported with deeper brine on shallow groundwater quality is likely to be much larger than that of the CO₂ and CO₂-induced geochemical reactions and in certain geochemical environment the reactivity of pure CO₂ will not be sufficient to mobilize metals beyond background levels.

HISTORY AND EVOLUTION:

LANL is one of the founding partners of ZERT and has been an active project participant since its inception. Within the framework of ZERT's focus on addressing science needs for evaluating efficacy of geologic sequestration as a U.S. strategy for minimizing the impacts of atmospheric carbon dioxide on climate change, LANL's overall approach has been to utilize a science-based prediction approach to develop capabilities to predict long-term performance of CO₂ sequestration sites and fill the science gaps that limits comprehensiveness of the prediction approach. LANL's initial SOPO was focused on establishing the scientific basis for predicting the performance of engineered geologic CO₂ storage sites, identifying key monitoring needs for such sites and identifying remediation strategies should a site exceed performance thresholds. The initial SOPO resulted in development of an initial system framework that linked system-level performance of an engineered geologic sequestration sites to key coupled processes/parameters at sites. The framework as well as monitoring and remediation needs were used to identify LANL activities in subsequent years. The second SOPO was focused on development of the first version of CO₂-PENS system-level model based on the framework developed during first year including linking the system level model to process-level models for

various parts of the sequestration system (such as reservoir, wellbores, faults, etc.). In addition, we initiated activities focused on understanding impact of CO₂ leakage on shallow aquifers through study of a natural analog at Chimayo, New Mexico as well as participated in the ZERT controlled release experiment. The third SOPO continued to build on the activities during the previous year including enhancing the capabilities in CO₂-PENS system model (incorporating Princeton's semi-analytical wellbore leakage model), Chimayo analog study and participation in ZERT release experiment. In addition, the SOPO also included other activities, including, development of numerical modeling capabilities for simulating CO₂-cement interactions and determination of feasibility of non-linear acoustic methods to detect cement integrity. In the following year, the focus of LANL SOPO shifted from developing system-level modeling capabilities to filling science gaps in fundamental science of CO₂-reservoir-rock interactions at geologic CO₂ storage sites. We continued our efforts at Chimayo analog site as well as participated in the ZERT release experiment. In addition, we also initiated activities focused on developing efficient numerical simulation capability for modeling wellbore leakage in LANL's FEHM simulator. In the following SOPO, we continued our efforts related to Chimayo study and ZERT release experiment. We also initiated activities related to enhancing the coupled flow-stress processes simulation capabilities in FEHM. LANL efforts through the years have led to a number of accomplishments ranging from enhancing our understanding of CO₂ interactions with geologic media to development of novel modeling capabilities to simulate processes resulting from large-scale CO₂ injection and predicting long-term performance of geologic CO₂ sequestration sites for risk assessment. We provide details for two major accomplishments below.

1. Development of CO₂-PENS framework and system-level model:

APPROACH: Large-scale implementation of geologic storage of CO₂ will require a large number of suitable storage sites (reservoirs). There is a need for a robust and reliable decision-making framework for evaluating the suitability of specific sites to ensure that they will perform up to required goals as well as to determine the risks associated with long-term storage of CO₂. The method needs to take into account the fundamental physical and chemical interactions resulting due to presence of CO₂ at multiple length and time scales and link fundamental scientific inputs to decisions based on a required performance goal. This means that a valid systematic approach will be required to limit site-specific evaluations to only the *critical factors* for the site (as opposed to all potential factors). We developed a framework and a coupled process-systems model based on the framework that can be used to study long-term performance of a wide range of geologic CO₂ storage sites utilizing the concept of *science-based prediction*. Science-based prediction links high level systems models, on which decisions can be based, to detailed models of physical and chemical processes by integrating theory, observation, experiment, and simulation. The foundation of predictions is built upon fundamental experimental (laboratory and field), theoretical and computational research into the behavior of individual subsystems and, as appropriate, the coupling between them. For some subsystems, the necessary information can be obtained from experimental data, but most of the complex subsystems involve an iterative approach among experiment, observation, theory and computation. Once an adequate understanding of the important subsystems is gained, the information is synthesized and simplified, accounting for uncertainties, and built into a systems model. The systems model accounts for all the

couplings between subsystems and their uncertainties, and produces a probabilistic prediction of the system behavior that can be used for decision-making. The key to the approach is how the transition is made between sub-systems level models and systems level models. For engineered geologic sites, this is done through probability functions that are developed explicitly or implicitly on detailed physics and chemistry. Site specificity is addressed by ensuring that the coupling of all possible performance controlling factors is included while recognizing that site particulars permit only a subset of all possible processes to be investigated in detail. This winnowing of processes is done systematically, providing confidence that the prediction for a site's performance has been comprehensive.

RESULTS AND DISCUSSIONS: Figure 1 shows an example high level systems model for a CO₂ sequestration project.

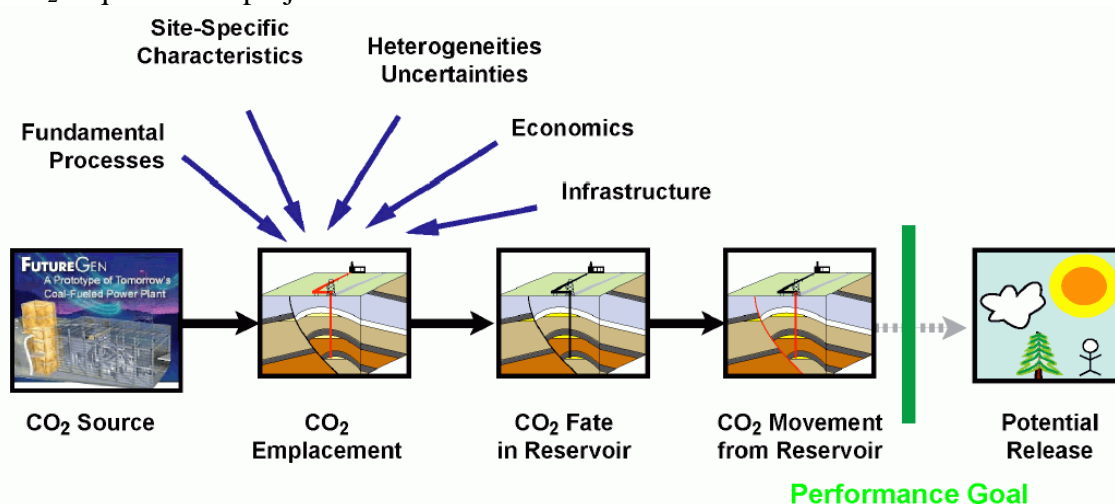


Figure 1. Schematic diagram showing a high level systems model for any CO₂ sequestration project.

A comprehensive model for any CO₂ sequestration project would include all the sub-systems, from the source for CO₂ such as a power plant, to the sub-systems affected by potential release of CO₂ such as the terrestrial environment near a geologic repository. Such a model can be used to analyze performance of any site based on any desired metric ranging from economics to health and safety. The sub-systems that make up the model shown in Figure 1 are themselves comprised of sub-systems. These lower level sub-systems can be further subdivided until the process levels are reached. The sub-systems which follow the “CO₂ Source” sub-system in Figure 1 represent the geologic repository and the environment in its vicinity. This is the main area of interest for long-term performance and risk assessment. The framework that can be used to study and analyze this area of interest is shown in further details in Figure 2. The main components of this framework include storage reservoirs, seals, potential release mechanisms, CO₂ transport beyond primary storage reservoir and CO₂ release at surface. This approach is effectively a graphical approach to the features/events/process (FEPs) method that has been demonstrated to be effective in addressing other engineered geologic systems. The framework described here can be used to predict fate of CO₂ in the reservoir. It can also be used to determine fate of CO₂ outside the primary reservoir in case of potential release from the reservoir. This provides the flexibility to perform both performance assessment and risk assessment calculations. The framework

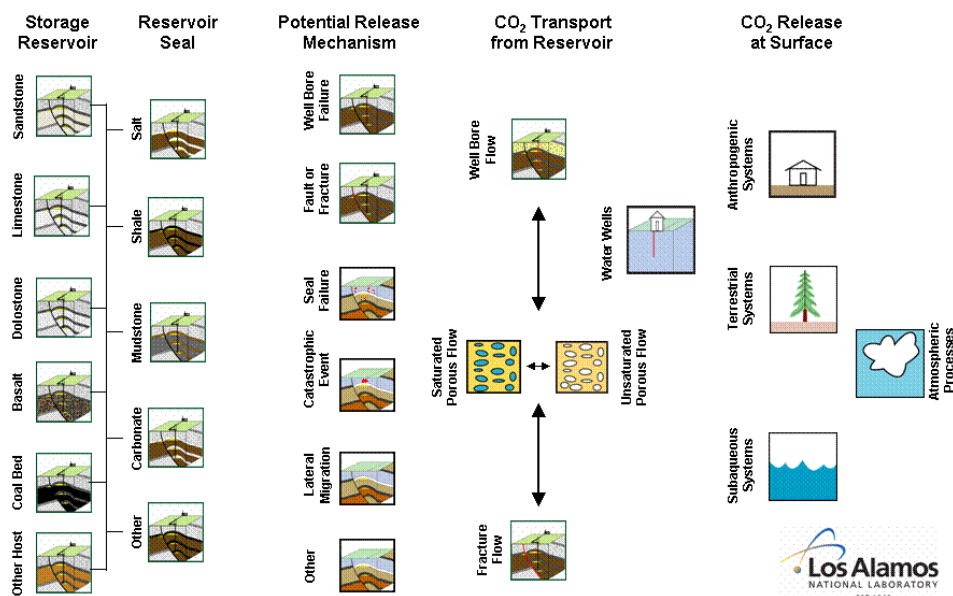


Figure 2. Framework for assessment of performance of an engineered geologic CO₂ storage site.

can be used to answer questions such as what is the ultimate sequestration capacity of the reservoir and what is the total injectivity of the reservoir. It can also be used to answer questions such as what is the probability of a wellbore failure at the sequestration site and in case of failure what are the consequences. Using the framework described above, we have developed a computational model using GoldSim® (Figure 3). GoldSim is a commercially available systems modeling package which has been tailored with the unique needs of engineered geologic systems in mind, particularly, uncertainty and heterogeneity. It can be linked directly to process level models such as reactive-transport codes.



Figure 3. First version of the GoldSim systems model, CO₂-PENS, developed at LANL.

The various boxes in the model represent various sub-systems shown in Figure 1. As described earlier the process level details are abstracted within individual boxes either through experimental observations, theoretical models or numerical simulations. Information on parameters including heterogeneity and uncertainty can be input using statistical distributions. This provides the systems model the ability to perform probabilistic predictions. The applicability of CO₂-PENS to sequestration site performance assessment has been demonstrated through multiple examples including at SACROC [Pawar, 2008 & Viswanathan et al, 2009]. Development of CO₂-PENS has continued through other projects but ZERT funding was instrumental in developing the solid foundation for follow-on work.

2. Understanding impact of CO₂ leakage on shallow groundwater:

APPROACH: One possible risk concern for geologic sequestration of CO₂ is impacts resulting from upward leakage through drinking water aquifers. Although CO₂ itself is not toxic, elevated CO₂ concentration could change the geochemical environment in the aquifer and cause aqueous and/or mineral precipitation/ dissolution reactions that might negatively impact drinking water quality. Modeling studies by Wang and Jaffe [2004] suggest that CO₂ leakage into potable aquifers has the potential to enhance trace metal dissolution. Although enhanced trace metal dissolution due to CO₂ has been observed at natural analogue sites such as Mammoth Mountain, CA, it is unknown how common this effect might be either in natural analogue sites or in engineered CO₂ storage systems. Studies of such impacts need to be performed in a broad range of aquifer types which will provide critical information for citing CO₂ storage facilities and adequately monitoring associated aquifers. We have used an integrated approach combining field data, laboratory experiments, and geochemical modeling, to determine if CO₂ fluxes have caused trace metal mobilization at a natural analogue site in Chimayo, New Mexico (Figure 4). Elevated CO₂ has been documented in several wells in the aquifer in the Chimayo area and is most notably evident in a cold geyser which has erupted through a shallow well twice daily for over 30 years. We have collected and analyzed a number of water samples from the region (Figure 4) to establish groundwater chemistry both in the regional aquifer (at the basin scale) and in the local Chimayo community.

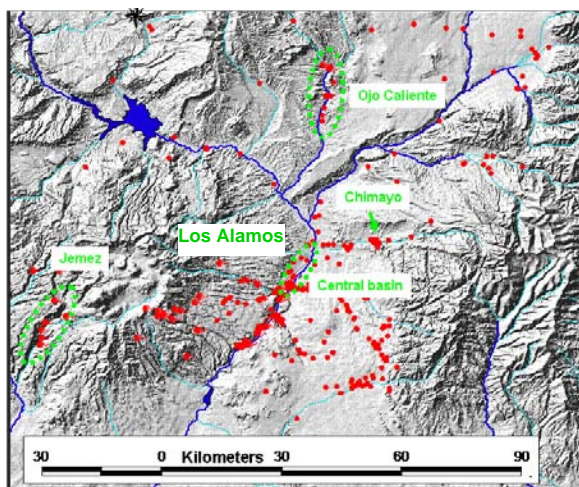


Figure 4. Location of wells and springs with groundwater chemistry data.

One trace metal commonly elevated in the regional groundwater is uranium, which is either derived from weathering of granitic clasts in the sediments, roll-front deposits, and/or volcanic ash beds. Sampling of regional ground waters (typically with very low $p\text{CO}_2$ values) has shown very high spatial variability in uranium concentrations, with some evidence that high uranium is associated with high alkalinity (but sometimes with low alkalinity) and with oxidizing environments. The geyser water itself is elevated in uranium, but is well within the background values for waters which are typically in the normal range of $p\text{CO}_2$ (< -2.0). Measured uranium concentrations in the geyser are far below saturation for common uranium minerals, suggesting uranium concentrations are limited either by slow dissolution kinetics or mineral availability or both. In a well near the geyser (also very elevated in $p\text{CO}_2$) uranium is below detection. There are several possible reasons for this, but clearly there are factors controlling uranium concentrations here and elsewhere in the area that are more much important than $p\text{CO}_2$. Based on this evidence, if sequestered CO_2 were to leak through a uranium-containing aquifer the impact on U concentrations would be very difficult to detect.

Although we have not found compelling evidence for CO_2 effects in this aquifer, there are clear impacts of co-solutes originating at depth with the CO_2 . For example, the CO_2 -enriched geyser water is also elevated in F, Na, Cl, and SO_4 . The origin of these co-solutes is unknown; possibly connate brines at depth or enhanced mineral weathering at depth due to the CO_2 plume. Processes occurring at depths well below the shallow drinking aquifers may cause contaminants to rise with the CO_2 and impact water quality through simple mixing. We used geochemical modeling and major ion data based on field sampling to establish simple reaction paths (some unknown combination of mixing, aqueous complexation, and mineral precipitation /dissolution reactions) that are consistent with measured trends in observed Cl concentration, $p\text{CO}_2$, and pH. The emphasis on these variables was due to the importance of Cl and $p\text{CO}_2$ in defining the degree to which CO_2 and brine has mixed with the aquifer; and pH is both an indicator of mineral reactions (especially with carbonates) and a master variable that will impact trace metal mobility. Second, use the established reaction paths to predict expected trends in trace metal concentrations and compare with measurements.

RESULTS AND DISCUSSIONS: Shallow groundwater in the vicinity of Chimayo is distinctive from other basin waters in that it is very high in dissolved CO_2 , higher in TDS and not as enriched with respect to sodium as the other relatively high TDS waters in the. High $p\text{CO}_2$ wells are clustered along a north-south trending fault (Figure 5). By calculating $p\text{CO}_2$ for all waters in the dataset, we compare the variability in $p\text{CO}_2$ within the Chimayo locality and the larger region. The Chimayo waters have anomalously high $p\text{CO}_2$ values. Regional waters have $p\text{CO}_2$ values somewhat higher than waters in equilibrium with the atmospheric ($p\text{CO}_2 = -3$), probably reflecting the consequence of mineral weathering (carbonates and/or silicates). Values as high as those measured in Chimayo waters can only be explained by invoking an internal source at depth. In Figure 6, we present the relationship between calculated $p\text{CO}_2$ (using PHREEQC) and measured Cl in Chimayo waters. Based on these data and assuming that the only source of Cl is deep connate brine and that Cl is a conservative species, we conclude that upwelling CO_2 is not always associated with deep connate brine (as it is in the Roberts Geyser). There are two distinct groups of high $p\text{CO}_2$ waters, one with background levels of Cl (shown in red, Group 2), one with high levels of Cl

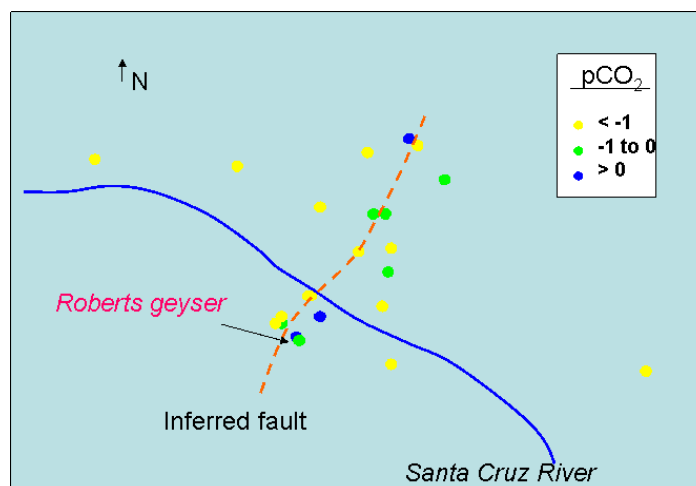


Figure 5. Map of wells in Chimayo. Color of dots indicate $p\text{CO}_2$.

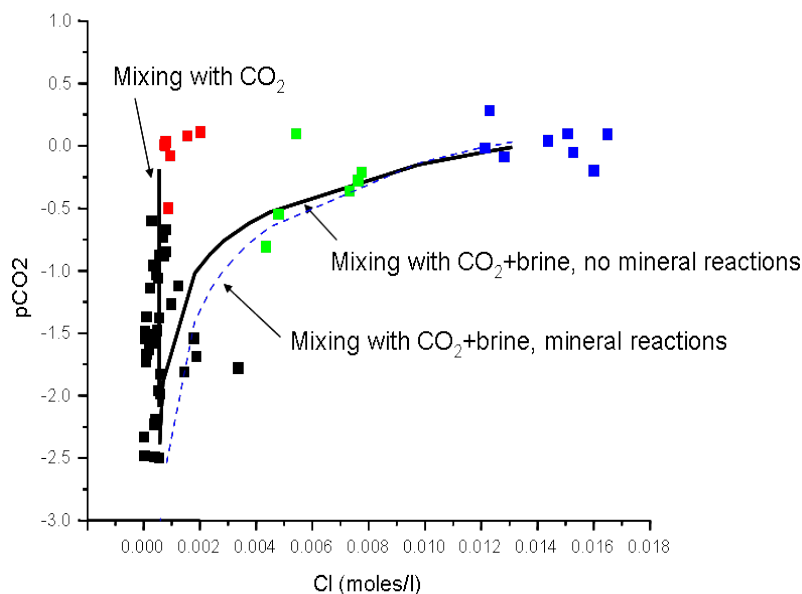


Figure 6. Measured variations in $p\text{CO}_2$ and Cl in Chimayo waters. Lines indicate reaction paths described in text.

(shown in blue, Group 4), and intermediate waters (shown in green, Group 3). Samples colored black (Group 1) represent background waters, minimally affected by either CO_2 or connate brine. We used geochemical modeling to determine the potential reaction paths that can help describe the observed data. We explored two reaction paths: diffusion of pure CO_2 into the shallow aquifer and migration of deeper brine/ CO_2 mix into shallow aquifer. Geochemical models using PHREEQC showed that the second reaction path matched the observed data better (Figure 7).

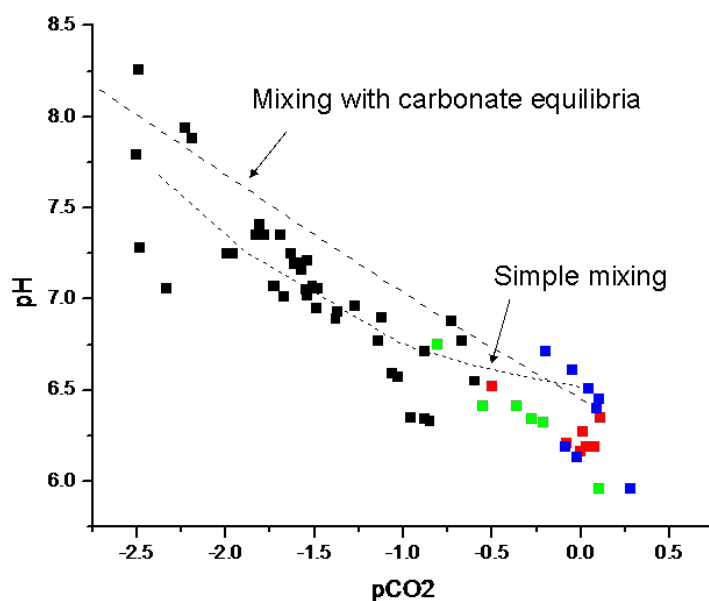


Figure 7. Measured variations in $p\text{CO}_2$ and pH in Chimayo waters. Lines indicate simulations of mixing with CO_2 -brine (geyser water) and background groundwater.

This model was used to examine the potential for uranium to be mobilized by the CO_2 plume. Roberts Geyser has measured concentrations of 160 ppb. This water is undersaturated with respect to common uranium minerals (see Table 1), suggesting the potential for uranium dissolution.

Table 1. Saturation indices with respect to common uranium minerals.

| | | |
|------------------------------------|-------|---|
| B- $\text{UO}_2(\text{OH})_2$ | -7.4 | $\text{UO}_2(\text{OH})_2$ |
| Coffinite | -8.7 | USiO_4 |
| Gummite | -12.5 | UO_3 |
| Rutherfordine | -5.4 | UO_2CO_3 |
| Schoepite | -7.2 | $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ |
| $\text{U}(\text{OH})_2\text{SO}_4$ | -26.4 | $\text{U}(\text{OH})_2\text{SO}_4$ |
| $\text{U}_3\text{O}_8(\text{c})$ | -19.5 | U_3O_8 |
| $\text{U}_4\text{O}_9(\text{c})$ | -29.4 | U_4O_9 |
| $\text{UO}_2(\text{a})$ | -13.0 | UO_2 |
| $\text{UO}_3(\text{gamma})$ | -9.7 | UO_3 |
| Uraninite(c) | -8.6 | UO_2 |
| Uranophane | -15.8 | $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2$ |

Furthermore, high alkalinity produced by CO_2 is known to complex U and further enhance U mineral solubility. Although available data for dissolved uranium at this site is very limited, examination of the data in the context of regional data and in the context of calculated saturation indices for common uranium minerals leads us to conclude that in the regional context there is no relationship between $p\text{CO}_2$ and [U] (see Figure 8), and furthermore, our highest $p\text{CO}_2$ sample (Roberts Geyser) has [U] concentrations which are elevated, but well within background levels.

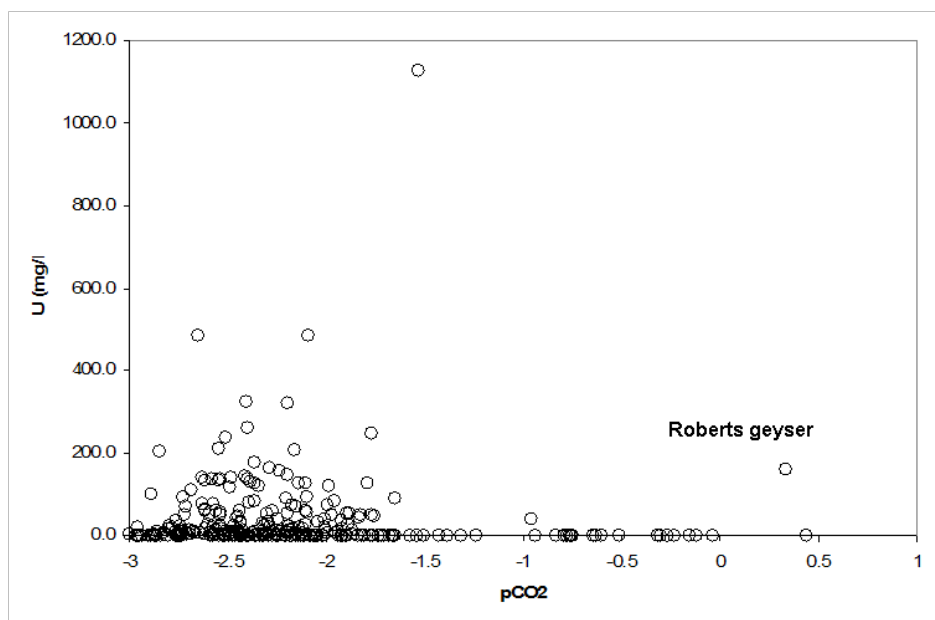


Figure 8. Measured variations in dissolved uranium and $p\text{CO}_2$.

Secondly, as the CO_2 /brine water mixes with background waters, $[\text{U}]$ is reduced from 160 ppb to below detection. This strongly suggests that any $[\text{U}]$ either transported upward with the CO_2 /brine or brought into solution locally by high $p\text{CO}_2$ concentrations can rapidly re-precipitate due to mixing with background waters or due to other non- CO_2 related processes.

CONCLUSION: In summary, we conclude based on geochemical modeling and available data that enhanced mobility of trace metals due to CO_2 is unlikely at this site. This study focused on groundwater in Chimayo, New Mexico, where high levels of dissolved carbon dioxide have been measured in shallow (< 200 ft deep) wells. We examined existing data for this site and regional groundwaters, supplemented the data with limited additional sampling in the vicinity of the high CO_2 waters, and conducted geochemical modeling to examine the potential impacts of mixing, aqueous reactions, and buffering due to carbonate mineral equilibrium on iron and uranium mobility. Results suggest enhanced trace metal mobility due to elevated CO_2 is either nil or too small to be detected within the context of natural background variability. Although the dataset presented and geochemical modeling do support our conclusion regarding trace metal mobility, it begs the basic question “are we not seeing effects because our sample size is so small” or, to phrase this another way, “if we collected more data or did a more exhaustive geochemical modeling study, would we begin to see clear trace-metal mobility effects?” Of course the honest answer is “yes, this is possible”, but is also true that neither the existing data nor geochemical theory suggest that this would be likely. The Chimayo site, in fact, shares many of the features that will cloud any natural analogue study of a CO_2 emerging through a shallow aquifer. At many sites, rather than emerging as pure CO_2 , the CO_2 is likely to rise with co-contaminants such as heavy metals (common in thermal waters), trace elements associated with residue from depleted oil reservoirs, and/or high levels of common ions (Na , Cl , SO_4 , etc.) associated with saline brines. The impact of these co-contaminants on shallow groundwater quality is likely to be much larger than that of the CO_2 and CO_2 -induced geochemical reactions, thus,

detection of a “CO₂” effect, per se, will be extremely difficult if not impossible. The Chimayo site offers one advantage in this respect; the data do show evidence of both “pure” CO₂ mixing with shallow waters and a CO₂-brine mixing with shallow waters. Geochemical modeling suggests pure CO₂ will be much more reactive, yet, in this geochemical environment the reactivity will not be sufficient to mobilize metals beyond background levels. If this result can be generalized to other sedimentary basin-fill aquifers (which are common in the arid southwest) it is encouraging for the prospect of carbon sequestration in this region.

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